

In general there is a region immediately around the parent peak that is free from artifacts of the deconvolution algorithm. As noted above, this region should extend from $(i_{max}-1)/i_{max} \times M$ to $(i_{max}+1)/i_{max} \times M$, where i_{max} is the maximum number of charges found on a molecule. In FIGS. 5 and 6 the boundaries of this region are marked by black triangles. In the deconvoluted cytochrome C mass spectrum (FIG. 7), however, a small peak (marked with an open triangle) is observed about 340 mass units higher than the molecular peak. Detailed examination of the measured spectrum reveals a small peak just above each main peak in the sequence whose position agrees with the peak found in the deconvolution. This observation indicates that the algorithm can readily detect small peaks close to a parent peak that may be due, for example, to parent species variants with slightly different masses.

This method for the determination of the mass of large molecules can also be applied when two or more parent species are present in the sample. FIG. 9 shows the mass spectrum for a solution of cytochrome C and myoglobin, each at a concentration of 0.5 mg/ml in an acidified mixture of acetonitrile, methanol and water. Also shown is the result of applying the deconvolution algorithm along with a "zoom" magnification of the pertinent parts of the deconvoluted spectrum. As might be expected, the number of different species that a mixture can contain and still be resolved by this procedure depends upon their relative concentration in the mixture and difference in their masses. The key factor is how close together are the peaks of the component multiply charged ions and whether the available analyzer can resolve them.

We claim:

1. A method of determining the molecular weight of molecules comprising the steps of:

generating a population of multiply charged ions from a distinct polyatomic parent molecular species, the number of charges on said ions defining the ion's charge state number, said population of ions comprising a plurality of sub-populations, the ions of each sub-population having the same charge state number, said population including one sub-population for each possible integral value of charge state number extending inclusively from a minimum of three to a maximum not less than five; carrying out a mass analysis of the ions in said population and from the results of said mass analysis obtaining mass/charge (m/z) values for said ions of said sub-populations; and determining a value of the molecular weight of said distinct polyatomic parent molecular species from the mass/charge (m/z) values of said ions of said sub-populations.

2. The method of claim 1, wherein said value of molecular weight of said distinct polyatomic parent molecular species is calculated by use of an averaging algorithm applied to the mass/charge (m/z) values of said ions of said sub-populations.

3. The method of claim 1, wherein said value of the molecular weight of said distinct polyatomic parent molecular species is calculated with a deconvolution procedure that transforms said mass/charge (m/z) values of said ions of said sub-populations into mass/charge (m/z) values that would be obtained by said mass analysis if all the ions of said distinct polyatomic parent molecular species were singly charged.

4. The method of claim 1, wherein said value of molecular weight of said distinct polyatomic parent molecular species is determined by averaging a set of values of molecular weight, each of said values of molecular weight in said set of values having been determined from the mass/charge (m/z) values of the ions from at least two different sub-populations of said plurality of said sub-populations.

5. The method of claim 1, wherein said minimum value of charge state number is not less than five and said maximum value is not less than ten.

6. The method of claim 5, wherein said value of molecular weight of said distinct polyatomic parent molecular species is calculated by use of an averaging algorithm applied to the mass/charge (m/z) values of said ions of said sub-populations.

7. The method of claim 5, wherein said value of the molecular weight of said distinct polyatomic parent molecular species is calculated with a deconvolution procedure that transforms said mass/charge (m/z) values of said ions of said sub-populations into mass/charge (m/z) values that would be obtained by said mass analysis if all the ions of said distinct polyatomic parent molecular were singly charged.

8. The method of claim 5, wherein said value of molecular weight of said distinct polyatomic parent molecular species is determined by averaging a set of values of molecular weight, each of said values of molecular weight in said set of values having been determined from mass/charge (m/z) values of the ions from at least two different sub-populations.

9. The method of claim 5, wherein the molecular weight of said distinct polyatomic parent molecular species is determined with a mass analyzer for which the nominal upper limit of molecular weight for singly charged ions is less than said molecular weight of said distinct polyatomic parent molecular species.

10. The method of claim 1, wherein the step of carrying out said mass analysis of the ions in said population produces a mass spectrum of ions, said mass spectrum comprising a sequence of peaks, each of said peaks having an m/z value corresponding to the m/z value of the ions of said distinct polyatomic molecular species in one of said sub-populations, and wherein the molecular weight of said distinct polyatomic parent molecular species is determined from the mass/charge (m/z) values of said peaks in said mass spectrum.

11. The method of claim 10, wherein the value of molecular weight of said distinct polyatomic parent molecular species is calculated by use of an averaging algorithm applied to the mass/charge (m/z) values of at least two of said peaks in said mass spectrum of the ions.

12. The method of claim 10, wherein the value of molecular weight of said distinct polyatomic parent molecular species is calculated with a deconvolution procedure that transforms said set of peaks in said mass spectrum, said set of peaks comprising one peak for each of said sub-populations of ions having the said same charge state number, into a single peak with a mass charge (m/z) value that would be obtained if all the ions of said distinct polyatomic parent molecular species were singly charged.

13. The method of claim 10, in which said ions of each of said sub-populations formed from said distinct polyatomic parent molecular species comprise at least two sub-species, each of said sub-species of ions having the same number of charges but a different combination